

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

B03

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>A61F 2/32, A61L 27/00, C08L 23/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/10953</b> <b>(43) International Publication Date:</b> 10 June 1993 (10.06.93)
<b>(21) International Application Number:</b> PCT/US92/10005 <b>(22) International Filing Date:</b> 25 November 1992 (25.11.92) <b>(30) Priority data:</b> 07/800,868 27 November 1991 (27.11.91) US <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). <b>(72) Inventors:</b> HOWARD, Edward, George, Jr. ; 844 Old Public Road, Hockessin, DE 19707 (US). CHAMPION, Allan, R. ; 506 River Road, Wilmington, DE 19809 (US). <b>(74) Agents:</b> FLOYD, Linda, Axamethy et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> BR, CA, JP, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ULTRAHIGH MOLECULAR WEIGHT LINEAR POLYETHYLENE, ARTICLES AND PROCESSES OF MANUFACTURE  <b>(57) Abstract</b>  Novel ultrahigh molecular weight linear polyethylene (UHMWLPE) in the form of a shaped article, exhibiting a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a prosthetic hip joint cup and as other prosthetic shapes for replacement of other joints of the human body. A novel process for preparing this article is also disclosed.		

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TC	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

TITLE

ULTRAHIGH MOLECULAR WEIGHT LINEAR POLYETHYLENE,  
ARTICLES AND PROCESSES OF MANUFACTURE  
5 CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. Serial No. 07/426,916 filed October 24, 1989 which in turn is a continuation-in-part of U.S. Serial No. 07/288,577 filed December 22, 1988, which in turn is a  
10 continuation-in-part of U.S. Serial No. 07/278,913 filed December 2, 1988.

BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to a novel ultrahigh  
15 molecular weight linear polyethylene (UHMWLPE). This novel UHMWLPE, in the form of a shaped article, exhibits in various embodiments a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a  
20 prosthetic hip joint cup and as other prosthetic shapes for replacement of other joints of the human body.

## 2. Description of the Prior Art

In U.S. Patent No. 3,944,536 (March 1976), Lupton et al. describe UHMWPE in the form of a fabricated  
25 article exhibiting an elastic modulus of 340,000 to 500,000 psi, a tensile impact strength of 140 to 600 ft lb/in<sup>2</sup>, a density of 0.95 to 0.98 g/cc at 25°C, a crystalline melting point of 142 to 148°C (as measured by differential thermal analysis) and a unique  
30 crystalline form characterized by the absence of fold spacings of 50-2000 Angstrom units (Å) and the presence of crystal spacings of about 10,000 Å. The critical feature of the process of producing this UHMWPE is disclosed to involve inducing crystallization of the  
35 molten polymer above 150°C by rapidly increasing the

applied pressure from an initial level of 1 to 1000 atmospheres to a second level of 2000 to 7000 atmospheres and then cooling rapidly while maintaining a pressure sufficient to maintain the polyethylene in the solid phase until the temperature is below the crystalline melting point of the polyethylene at atmospheric pressure.

In Kunststoffe German Plastics 77 (1987) pp. 617-622, in an article entitled "Ultrahigh Molecular Polyethylene for Replacement Joints", Eyrer et al. point out that the service life of joint replacements made of UHMWPE is limited. Analysis of the damage to over 250 explanted hip cups and tibial plateaus revealed a changed property profile which they explained by post-crystallization resulting from oxidative chain decomposition. They suggested optimizing the processing of polyethylene under higher pressure and higher temperature to increase the degree of crystallinity. The Eyrer et al. product displays a creep of above 5% at a compression of 1000 psi (6.9 N/mm<sup>2</sup>) for 24 hours at 37°C.

One of the most remarkable advances in the medical field in recent years is the development of prosthetic joints, particularly the load bearing hip. The crippled and sometimes bed ridden elderly can walk again. The key to this development is UHMWPE because, not only does it have the necessary impact strength, but it initiates no adverse blood reactions. But at present, these prosthetic joints are limited to the older, less active segment of the population because the polymer tends to creep under the pressure that a younger more active person might develop while involved in recreation or employment. The creep would cause the loss of the close tolerance required between the plastic socket and the polished metal ball attached to the femur. These changes in dimensions disturb the distribution of

walking forces which in turn accelerates more creep and wear. Eventually the increased pain requires a traumatic revision operation. One objective of this invention is to provide UHMWPE prosthetic joints with improved creep resistance hence removing some of the age restriction existing on the present polyethylene joints. This invention can also function in other UHMWPE-based prosthetic devices, for example, non-conforming joint assemblies such as knees which require a special balance of properties, especially with respect to tensile modulus and creep resistance.

#### DESCRIPTION OF THE INVENTION

An object of this invention is to provide tough ultrahigh molecular weight linear polyethylene (UHMWLPE) compositions and shaped articles therefrom which exhibit unusually low creep and have excellent tensile flexural properties.

UHMWLPE compositions of this invention have molecular weights of at least 400,000, preferably at least 1,000,000. Those UHMWLPE of this invention that are prepared by processing at elevated pressure also have two crystalline melting points, the higher of which is greater than 144 degrees C (as measured by differential scanning calorimetry) and the reduction in said higher melting point upon remelting being greater than 11°C, an infrared crystallinity index of at least about 0.28, preferably at least 0.35, and are characterized by a crystal morphology comprising a bimodal distribution of molecular chain fold spacings, one group of said spacings being greater than 2000 Angstroms reflecting a population of very highly extended molecular chains, the other group being less than 500 Angstroms.

One embodiment of such UHMWLPE compositions exhibits a flexural modulus of 250-500 kpsi, a tensile

stress at yield of 3.5-4.5 kpsi, a tensile stress at break of 4-9 kpsi, a tensile modulus of 250-700 kpsi, an elongation of 200-500%, a notched Izod impact resistance of 12-25 ft.lb. per in. of notch, a creep at a  
5 compression of 1 kpsi of less than 1.4% after 24 h at a temperature of 23°C and a relative humidity of 50%. This product is prepared in a process consisting essentially of following steps:

(a) forming, by milling or casting or the  
10 like the article from UHMWLE having a molecular weight of 400,000, preferably at least 1,000,000 and most preferably at least 6,000,000;

(b) placing the article in a pressure vessel (e.g., an autoclave) substantially filled with a fluid  
15 that is inert to the article, preferably water, heating the vessel to a temperature of at least 190°C, preferably 200°-260°C, raising the pressure in the vessel, usually by adding more fluid, to at least 200 MPa, and maintaining the temperature and pressure for at  
20 least 0.5 hour, preferably at least one hour;

(c) thereafter, cooling at a slow rate by reducing the temperature to about 160°-170°C or below, preferably to 160°C or below, most preferably to below 140°C, while maintaining a pressure of at least 200 MPa,  
25 the rate preferably at least 300 MPa, the rate of cooling being such that temperature gradients in the shaped article are substantially avoided; and

(d) cooling to a temperature of about 130°C or below, preferably below 120°C, most preferably below  
30 100°C, and reducing the pressure to about 100 kPa, either sequentially or simultaneously, in a manner such that remelting of the article is prevented.

Alternatively in step (b), the article, fluid, and reactor are heated to about 200-230°C, the pressure is  
35 applied and the system held at this temperature while

polymer slowly loses heat of crystallization and solidifies. Also, the pressure can be applied at any temperature during the heating cycle if the temperature exceeds about 200°C. Moreover, the pressure vessel can be used more efficiently by preheating polymer outside the reactor because heating polyethylene is a very slow process due to its high heat of fusion and thermal insulating property. The polymer can be heated in an oven, preferably in an inert atmosphere to prevent oxidation, particularly when the temperature is above 160°C. Because the UHMW polyethylenes do not flow when melted, they can be handled while hot and transferred to the preheated pressure vessel without deforming.

In step (c), the polymer must be cooled slowly at the high pressure until it is fully crystallized. At 300 MPa pressure, the crystallization temperature of UHMWLPE of over 1,000,000 molecular weight is in the range of 170°C-190°C. The pressurized vessel should be cooled slowly to insure that the temperature of the polymer is not significantly above the vessel temperature, particularly if the pressure vessel construction does not permit means for measuring the temperature of the polymer itself. It is also very important in step (c), to cool in a manner that limits or avoids severe temperature gradients in the article. For example, for a 1 inch X 6 inch rod, a cooling rate of about 10°C per hour is usually necessary. Although cooling rates no greater than 10°C per hour are preferred, cooling rates as high as about 35°C per hour have been used to provide the product of this invention. However, these latter rates require careful control in order to limit temperature gradients during cooling. Cooling rapidly, as taught in the prior art, will not provide the article of this invention. This invention is particularly useful for manufacturing shaped articles

where temperature gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch, usually for joints at least 1 inch x at least 2 inches. Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch, i.e., at least 0.2 inch in thickness. It has been found that in such articles, the temperature gradients must still be controlled by the process of this invention in order to obtain the product of this invention.

In step (d), cooling the polymer to a temperature below its melting point at any particular pressure is necessary to ensure that none of the polymer melts as the pressure is reduced, since lowering the pressure lowers the melting point.

As an optional fifth step, it is advisable to shave the surface of the article, i.e., remove approximately the outer 2 millimeters that might contain any fluid-affected polymer.

Products of the aforementioned process possess superior strength properties and resistance to creep under load, and are excellent materials for orthopedic replacement parts.

In addition to utility in the field of orthopedic replacement, the products prove useful in other applications also requiring the special properties of the products. Not only shaped articles are of interest, but also films and fibers as well as other "downstream" forms and unshaped granular forms of the product will prove useful. Film formed of the product of Example 5 is exemplified in Example 13. These examples are illustrative only, and other forms, shaped and unshaped, of the present products are contemplated within the



scope of the invention. Therefore, "article" shall include both shaped articles and unshaped articles.

By "fluid" in the processes of this invention, is meant a liquid, vapor or gas that is inert to process conditions and does not adversely affect, or is prevented from adversely affecting, the UHMW polymer being processed. It has been found during manufacturing the product of this invention that use of a gaseous fluid can be beneficial. Specifically, in the above-described process, the shaped article formed from commercially available UHMWLPE in step (a) is placed (step (b)) in a pressure vessel containing a gaseous fluid, for example, argon. When argon is used, penetration of the gas into the polymer should be prevented by surrounding the UHMWLPE article with a thin stainless steel or similar metal container as described in copending U.S. Serial No. \_\_\_\_\_ to S. Li et al., filed on March \_\_\_\_\_, 1990, which in turn is a continuation-in-part of U.S. Serial No. 07/426,918 to S. Li and Howard, filed on October 24, 1989 which in turn is a continuation-in-part of U.S. Serial No. 07/288,576 filed December 22, 1988 which in turn is a continuation-in-part of U.S. Serial No. 07/278,912 filed on December 2, 1988. As previously mentioned, other gaseous fluids may be used in place of argon so long as they do not adversely affect, or are prevented from adversely affecting, the polymer and are otherwise inert under process conditions.

After placing the suitably protected polymeric article into the gas-containing pressure vessel, a pressure of at least 200 MPa is applied and the vessel is heated to about 220°C for about 6 hours. Thereafter, the temperature is "ramped" down at a rate no greater than about 10°C per hour to about 160°C while maintaining the pressure above 200 MPa. The temperature

is then "ramped" down at a maximum rate to 50°C while maintaining the high pressure, after which the pressure is released.

Also provided by this invention is an ultrahigh  
5 molecular weight polyethylene having a molecular weight of at least 400,000, preferably at least 1,000,000, a normal folded chain crystal morphology, and exhibiting a flexural modulus of 150-300 kpsi, a tensile stress at yield of 3.5-4.3 kpsi, a tensile stress at break of 4-6  
10 kpsi, a tensile modulus of 150-300 kpsi, a notched Izod impact resistance of 15-25 ft.lb. per inch of notch, an elongation at break of 200-1400%, a creep at compression of 1 kpsi of less than 2% after 24 h at a temperature of 23°C and a relative humidity of 50% and an infrared  
15 crystallinity index of at least about 0.35. This polyethylene is prepared by heat treatment without application of pressure in a process comprising the following steps:

(a) forming by milling a casting or the like,  
20 the article from UHMWPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000;

(b) subjecting said article to a temperature of 280°-355°C, preferably 320°-355°C, for at least 0.5 hour, preferably at least 3 hours, in an inert  
25 atmosphere; and

(c) cooling the article non-precipitously to a temperature of about 130°C or below. As in the other embodiments, the rate of cooling is such that temperature gradients in the shaped article are  
30 substantially avoided. The product of this non-pressurized embodiment is particularly useful for manufacturing shaped articles where temperature gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at  
35 least 1 inch x at least 1 inch, usually for joints at

least 1 inch x at least 2 inches. Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch, i.e., at least 0.2 inch in  
5 thickness.

The thermally heated, unpressurized product still in the folded chain form has improved elongation, crystallinity and impact resistance over the starting material. Preferred embodiments exhibit elongation at  
10 break of up to about 1400% (Example 11). However, the folded chain products are not equivalent to the enhanced, pressurized forms of UHMWLPE of this invention.

As already indicated, a very important property of  
15 the products of this invention is creep resistance. For prosthetic devices, e.g., knee, hip, elbow joints, etc., any substantial creep can be devastating in the loss of the benefits of extremely expensive surgery. For some applications, still lower creep, higher stiffness,  
20 higher elongation, and particularly higher tensile strengths at yield are necessary. It has been found that products having these properties can be obtained by inserting between steps (a) and (b) in the four-step pressurized process described herein above a preliminary  
25 step wherein the starting UHMWLPE is heated to a temperature of 280°-355°C, preferably 320°C-355°C, at atmospheric pressure in an inert atmosphere for at least 0.5 hour, preferably at least 3 hours. The polymer should be heated as near as possible to, without  
30 reaching, its decomposition temperature. The hot polymer should be cooled slowly because very rapid cooling, such as immersion in cold water, causes internal voids to form. Voids result from a combination of large volume change (about 30%) on melting and poor  
35 heat conductivity in polyethylene. It is convenient to

allow the polymer to cool wrapped in insulation. The hot polyethylene can be placed directly into the hot pressure vessel, or first cooled, then reheated to the normal 200°C and placed in the pressure vessel.

- 5        Alternatively, these enhanced properties can be attained by subjecting the above-described folded chain product of the invention to steps (b), (c) and (d) of the pressurized process.

10        The polyethylene product prepared as just described from either the folded chain product or from conventional UHMWLPE having a molecular weight of at least 400,000, exhibits a flexural modulus of 250-650 kpsi, a tensile stress at yield of 3.5-5.4 kpsi, a tensile stress at break of 4-6 kpsi, a tensile modulus  
15 of 250-700 kpsi, a notched Izod impact resistance of 12-25 ft.lb. per inch of notch, an elongation at break of 200-600%, a creep at compression of 1 kpsi of less than 1.4% after 24 h at a temperature of 23°C and a relative humidity of 50% and an infrared crystallinity  
20 index of at least about 0.28, preferably at least 0.35. The product is further characterized by having a crystalline melting point of greater than 144°C, the reduction in said melting point upon remelting being greater than 11°C, and a bimodal distribution of fold  
25 spacings, one group of said spacings being greater than 2000 Angstroms, the other group being below 500 Angstroms.

30        Certain preferred embodiments of this product of the invention have tensile moduli of at least 350 kpsi, and a creep value of less than 0.6%.

It is envisaged that the additional preliminary step of heating the starting UHMWLPE to 280°-355°C will also provide superior characteristics to the product described by Li.

By inert atmosphere in the processes of this invention is meant a gaseous or vaporous environment that is stable and inert to process conditions.

Suitable gases include nitrogen and the noble gases.

- 5 Suitable vapors include those of nonflammable, chemically inert and thermally stable liquids such as the perfluoroalkylpolyethers (Example 10). Vacuum may also be employed but is not preferred.

For purposes of this invention, ultrahigh molecular  
10 weight linear polyethylene (UHMWLPE) is defined as a linear polyethylene having an estimated weight-average molecular weight greater than about 400,000, usually 1,000,000 to 10,000,000 as defined by a melt index (ASTMD-1238) of essentially zero and a reduced specific  
15 viscosity (RSV) greater than 8, preferably 25-30. The relationships of RSV to intrinsic viscosity and to molecular weight are those developed by R. Chaing as presented by P. S. Francis et al. in J. Polymer Science, 31, 453 (1958).

- 20 Another characteristic property of the products of this invention is their infrared crystallinity index (IRCI). This property, which fairly accurately reflects product crystallinity, is higher than in conventional UHMW polyethylene. To determine this index, samples are  
25 first obtained by microforming thin sections. Heat should be avoided during preparation of the samples. ICRI is the ratio of the band at 1894 reciprocal centimeters ( $\text{cm}^{-1}$ ) to the band at 1305 reciprocal centimeters ( $\text{cm}^{-1}$ ). Since the band at 1894  $\text{cm}^{-1}$  is  
30 attributed to the crystalline nature of the material and the band at 1305  $\text{cm}^{-1}$  is attributed to its amorphous nature, ICRI increases as the crystallinity increases. The product of this invention displays an IRCI of at least about 0.28, preferably at least 0.35. In fact,  
35 values of 0.73 and higher have been obtained. On the

other hand, IRCI values for prior known UHMWLE's seldom reach above 0.3.

The invention will be more clearly understood by referring to the drawings and examples, which follow.

5 In the drawings, Figure 1 is a schematic diagram of the equipment used in the process for forming the product of the invention using argon gas; and Figure 2 is a schematic diagram of the equipment used in the hydrostatic process.

10 In the examples, most of the properties are measured using standard ASTM tests.

All of the physical measurements were carried out under constant humidity (50% relative humidity) and temperature (23°C) conditions.

15 Tensile modulus, ultimate tensile strength, yield strength and elongation were measured according to ASTM D-638 with the following modifications:

- samples machined into shape without lubricating fluid
- 20 • type I tensile bar
- cross head speed = 0.2"/min for tensile modulus  
2.0"/min for tensile stress and elongation.

25 Resistance to deformation (creep) was measured in accordance with ASTM D-621 with the following modifications:

- samples machined into cylinders or cubes without the use of lubricating fluids
- 30 • samples measured 0.5" x 0.5" x 0.5"

Flexural properties were measured according to ASTM D-790 with the following modifications:

- samples machined into shape without the use of lubricating fluids

- typical flex bar measures 0.125" thick x 0.5" width x 5" length
- span or gage is 2.0". (This was determined by a span/depth ratio of 16/1.)
- 5       • cross head speed = 0.05"/min (calculated based on span).

Impact resistance was measured using the notched Izod test given in ASTM D-256 with the following modifications:

- 10       • samples machined into shape without the use of lubricating fluid
- type A or notched IZOD
- specimen size is 0.5" x 2.5"
- 0.4" from bottom of vertex to opposite side
- 15       • 1.25" impacted end (from end of bar to vertex of notch)
- the notch should be the specified angle of 22.5 degrees.

It should be appreciated that in all embodiments of the invention the step of forming the article by milling, casting, or the like from UHMWLPE may be performed as the first step in the process (i.e., before heating or preheating) or as the last step in the process (i.e., after the cooling step).

25       The following non-limiting examples, including the improved and superior embodiments, illustrate the basic principles and unique advantages of the present invention. Various changes and modifications may be made without departing from the spirit and scope of the present invention.

#### EXAMPLE 1

The material used in this example is American Hoechst Hostalen 415 GUR ultrahigh molecular weight polyethylene. It was obtained in the form of bars, 3" in diameter and up to 5' long in length. The material

will be referred to as UHMWLPE. The molecular weight was 4-6 million.

One or more pieces of the UHMWLPE 11 were placed into stainless steel, seamless, 48" long cylinders or sleeves 12. The thickness of the stainless steel was 1/8". The bottom of the cylinders was closed by welding a stainless steel cap 13 onto the bottom of the cylinder. The top of the cylinder was partially closed by welding on a modified cap 14 which contained a vacuum port 15. The cylinder was then evacuated using a vacuum pump and sealed by crimping the port to form a can that surrounds the piece of UHMWLPE completely. The sealed cylinder was then placed in a containment vessel 16 large enough to hold 15 cylinders. The containment vessel 16 was then placed into a hot isostatic pressing (HIP) unit 17 with molybdenum heating units 18. Thermocouples were added to monitor the temperature of the cylinders.

The basic function of the HIP process is to uniformly heat a load while applying pressure uniformly to all surfaces. The pressure medium used in this case was argon. The UHMWLPE is protected from contact with the argon by the stainless steel cans.

The process conditions were:

1. Apply pressure to 39,000 psi (269.1 MPa).
2. Heat to 220°C.
3. Hold for 6 hours at 220°C and a minimum pressure of 41,000 psi (282.9 MPa).
4. Ramp temperature down at a rate no faster than 10°C per hour to 160°C. Pressure is maintained above 41,000 psi (282.9 MPa) during this time.
5. Ramp temperature down at maximum rate to 50°C while maintaining the pressure above 41,000 psi (282.9 MPa).



6. Below 50°, pressure may be let down and the cycle ended.

The UHMWPE rods were then removed from the sleeves and parts were fabricated for physical testing. It is noted that the material produced exhibits much higher tensile modulus, flex modulus, melting point, density and creep resistance than the starting material (Control A).

Material	DSC Melting Point (°C)	Density (grams/cc)	IRCI
Control A	137.0-140.7°C	.93-.94	0.24
Example 1	148.0-152.0°C	.947	≥0.45

<u>Properties</u>	<u>Control A</u>	<u>Example 1</u>
-------------------	------------------	------------------

Tensile (ASTM D638)

Modulus, kpsi	185	315
Stress, break, psi	4500	4688
Stress, yield, psi	3476	4082
Elongation, brk, %	262	227

Flexural (ASTM D790)

Modulus, kpsi	165	291
---------------	-----	-----

Deformation (creep) (ASTM D621)

Load, psi		
500	0.5	0.3%
1000	1.6	0.7
2000	5.9	2.4

10 Additional evidence of the products' distinctiveness is found in data produced by small angle X-ray testing. A truly characteristic small-angle X-ray scattering plot of desmeared intensity (by the method of P. W. Schmidt, Acta Cryst., 13, 480 (1960) and Acta Cryst., 19, 938 (1965)) ( $I \times (2 \theta)^2$ ) versus scattering angle ( $2 \theta$ ) for the material of the invention exhibits two distinct scattering peaks associated with crystal long-spacings in the range of 480 angstroms (at  $2 \theta = .184$  degrees) and 4610 angstroms (at  $2 \theta = .0192$  degrees). The presence of

the sharp diffraction peak at the lower angle is indicative of an extended polymer chain conformation (with a lamellar thickness greater than 2000 angstroms) whereas the more diffuse higher-angle peak corresponds to a lamellar thickness characteristic of conventional folded chain PE. This provides clear evidence for the presence of two scattering peaks in the subject invention material which correspond to lamellar thicknesses both above and below 2000 angstroms. By comparison, the previously patented extended chain polyethylene of Lupton et al., was reported to exhibit a complete absence of any detectable small angle X-ray scattering in the range of 50 to 2000 angstroms. Consequently this work demonstrates that the subject invention material is morphologically distinguishable from Lupton et al.

#### EXAMPLE 2

The material used in this example is an ultrahigh molecular weight polyethylene obtained from Jet  
20 Plastics, Inc.

A rod 21 measuring 6" x 1 1/8" was placed in the cavity 22 of a stainless steel, seamless, cylindrical reactor 23. The cavity 22 had a diameter of 1.35" and was about 9" long.

25 Water was fed into the cavity 22 at the entry port 24 through the use of a high pressure water pump 25 powered by compressed air. Simultaneously, the reactor was heated by electrical heaters 26 surrounding the reactor.

30 In the first step, the rod 21 was heated to a temperature of 220°C under a hydrostatic pressure of 200 MPa. The pressure was raised to 300 MPa while the temperature was maintained at 220°C for 2 hours. The temperature was permitted to fall to 209°C over another  
35 2 hour period, and then to about 182°C in 4 hours.

Finally, the rod was cooled to 49°C by subjecting the reactor 23 to compressed air from the blower 27 over a period of one hour and the pressure released.

The rod was removed from the reactor and the surface was shaved. The product, a sample taken substantially from the center of the rod, displayed a DSC melting point of 154.5°C, and, on reheating, a DSC melting point of 140°C.

The material, when subjected to a compression pressure of 1000 psi for 24 hours at a temperature of 23°C and a relative humidity of 50% in accordance with ASTM D-621, deformed only 0.4%.

The other properties of the product were:

flexural modulus	- over 250 kpsi
tensile modulus	- over 300 kpsi
tensile stress (yield)	- over 3500 psi
tensile stress (break)	- over 4000 psi
elongation (break)	- less than 500%.

Its infrared crystallinity index was over 0.5.

The hydrostatic process described in Example 2 is the best mode for preparing the product of this invention. This process has important advantages. The pressure transfer liquid, water, is non-toxic and inexpensive. The hydraulic pressure is applied equally in all directions resulting in a substantially homogeneous product. This compares to processes shown in the prior art where hydraulic pressure is applied by a piston or a ram. In these latter cases, the high shrinkage polymer tends to solidify along the heat-escaping walls making it difficult for the pistons to advance and still apply the pressure uniformly. The result is a heterogeneous product.

It should be understood that although water is the preferred liquid fluid to use in the process, other liquids, with the same criteria as mentioned for gases,

are also useful. Thus, methanol, ethanol, glycerin, glycols, etc. in addition to various aqueous solutions may be used.

The salt selected for an aqueous solution may be one that imparts a desirable property to the surface of the shaped article.

#### EXAMPLE 3

This experiment was carried out in a manner similar to Example 2 except that the pressure in the first step was 300 MPa. The material was maintained at 220°C under 300 MPa for 4 hours. The temperature was allowed to fall to 190°C over an 8-hour period. After which, it was cooled to 100°C in 1 hour.

Samples were taken from 1/8" inside both ends of the rod and had melting points of 150.8°C and 153.2°C. When reheated, the melting points were 135.5°C and 138°C, respectively.

The infrared crystallinity index was 0.791; and the creep, when measured in accordance with ASTM D-621, was less than 1%. These measurements were obtained on a sample taken from the center of the rod.

#### EXAMPLE 4

The experiment was also carried out in a manner similar to Example 2 except for the following changes in the heating/cooling cycle:

Heat at 211°C and 300 MPa  
and maintain for 1 hour;  
Cool to 200°C in 1 hour at 300 MPa;  
Cool to 180°C over 5 hours at 300 MPa  
(cooling rate 200 → 180°C, 4°/hour); and  
Cool to 33°C in 1 hour and 3 minutes.

The product from inside both ends melted at 150°C and on reheating, at 135.5°C. The product, when tested in accordance with ASTM D-621 displayed a creep of less than 1%. Its infrared crystallinity index was 0.652.

EXAMPLE 5

A reactor with the general configuration shown in Figure 2 having an internal diameter of 4" and being 22" long, was charged with a 3 1/8" x 18 1/16" rod of UHMWPE (made from polymer from American Hoechst, Hostalen GUR 415). The closed vessel was evacuated, filled with water, and heated to 232°C at which point the pressure was increased to 300 MPa with the water pump. This pressure was maintained until the end of the experiment. The reactor was held between 210 and 230°C for 3 hours, cooled over 1 hour to 200°C, cooled to 175°C in 5 hours (5°/hour) and then cooled to 80°C in 7 1/2 hours.

The resulting product rod was still in a cylindrical form with very little warpage. It measured 3 1/8" x 17 15/16". End pieces, 1/2" thick, were cut off each end of the rod revealing a uniform white color. Samples taken from the center of the rod on these cuts gave melting points of 152.9°C (201 J/g) and 152.1°C (207 J/g) when heated at 20°C/minute. When reheated, the melting points were 137.5°C.

A six inch section of the rod was sawed into 3/16" thick shapes for physical tests, then carefully milled to remove saw marks to 1/8" thickness. The resulting polymer had the following properties:

25	IZOD	18.7 ft. lb./in. of notch
	Flexural Modulus	298.9 kpsi
	Tensile Properties	
	Stress at yield	4190 psi
	Stress (at break)	5430 psi
30	Elongation	280%
	(at break)	
	Modulus	378.3 kpsi
	Creep (at 1000 psi load)	0.6%
35	All tests at room temperature.	

The crystallinity index (IRCI) was 0. 528.

#### EXAMPLE 6

In this example, the product was prepared with an exceedingly smooth surface.

5       A polished brass disk, about 1 1/2" diameter, 1/4" thick was pressed at 160°C against a UHMW polyethylene plug. The combination was cooled under pressure and sealed in a heat shrinkable Teflon FEP™ tube. The polyethylene was converted in a hydrostatic system by  
10 this procedure in the vessel used in Example 5.

The heating, cooling cycle was as follows:

300 MPa and 210°C in 1 hour;

300 MPa 210°C to 200°C in 1 hour;

300 MPa 200°C to 178°C in 6 hours, 45 minutes;

15       and

300 MPa 178°C to 23°C in 2 hours, 20 minutes.

The polyethylene did shrink so that it had a smaller diameter than the disk, but the polymer stuck to the surface. When forced apart, the surface was  
20 extremely smooth.

This technique is important in preparing complicated surfaces where smoothness is extremely important, such as on bearing surfaces such as medical prosthesis for knee and hip joints, or bearings for  
25 motor shafts, etc. Machine cutting polymers always leaves very small ridges.

#### EXAMPLE 7

The reactor of Figure 2, internal diameter 4" by 22" long was charged with a 3" x 18" rod of American  
30 Hoescht, Hostalen GUR 415 ultrahigh molecular weight polyethylene, water, and a nominal pressure of 100 psi (690 kPa). The system was heated to 170°C to 176°C and held there for 1 hour, then the pressure was raised to 300 MPa. The temperature was maintained at 179°C-174°C  
35 for 3 hours, during which time the polyethylene

crystallized. The reactor was cooled to 79°C in 1.7 hours.

Two samples were taken; one from the center of the rod and another 1/2 inch from the outer surface of the rod. The melting points, as measured by DSC, were 150.9°C and 150.4°C, respectively, and upon reheating, 136.6°C and 137/3°C. Thus, the increases in melting points were 14.3°C and 12.7°C, respectively. The infrared crystallinity index was 0.5.

10 EXAMPLE 8

This example shows that the polymer can be cooled at a rate as high as 34.5°C per hour in the critical cooling step (step 5) if proper precautions are taken to limit temperature gradients.

15 A one inch rod of UHMWPE from Jet Plastics, Inc. was used. It was placed in the pressure vessel with water and subjected to the following treatments:

300 MPa and 220°C for 2 hours;  
300 MPa, cool to 200°C in 50 minutes;  
20 300 MPa, cool to 177°C in 40 minutes;  
300 MPa, cool to 35°C in one hour.

A test sample taken one-half inch from the end of the rod and in the center displayed a DSC melting point of 153.8°C, and, on reheating a DSC melting point of 139.7°C.

The material, when subjected to a compression pressure of 1000 psi for 24 hours at 23°C and a relative humidity of 50% in accordance with ASTM D-621 deformed 0.5%.

30 EXAMPLE 9

Superior Enhanced UHMW Polyethylene prepared by Preheating Polymer to 325°C.

A 3-1/16" x 15" rod of UHMW polyethylene (Hoechst GUR415, fabricated by PolyHi) was heated to 325°C in an atmosphere of N<sub>2</sub> for six hours. The hot rod was quickly

placed in a pressure vessel preheated to 212°C. The vessel was sealed immediately and pressured with water to 300 MPa. The cooling schedule was as follows:

- 5           212° to 191°C 65 minutes  
           191° to 181°C 63 minutes  
           181° to 175°C 2 hours  
           175° to 174°C 6 hours, 26 minutes  
           174° to 45°C 3 hours, 15 minutes

10           The rod was cut into test samples and analyzed with the following results:

DSC (Differential Scanning Calorimetry)

	<u>Center of Bar</u>	<u>1 cm from Bar Edge</u>
<u>m.p., °C</u>		
1st heat	150.5	152.4
2nd heat	137.9	139.0
$\Delta T$	12.6	13.4

Heat of Fusion

1st heat	198.8 J/g
2nd heat	134.4 J/g

Infrared Crystallinity Index

(Samples cut from within 5 mm of bar edge)

In Bar Direction	0.613
Perpendicular to Bar Direction	0.633

Flex Modulus, (kpsi)

424.0  
 386.1

Deformation (Creep) (% at 1000 psi load)

In Bar Direction	0.4
Perpendicular to Bar Direction	0.6

Density g/ml

Gradient column	0.9595
Infra Red	0.957, 0.958



Tensile Properties:

	In Bar Direction (6" Test Bars) (Type I)	Perpendicular to Bar Direction (2-1/2" Test Bars) (Type V)
<u>Stress, psi</u>		
Yield:	4743	4516
	4758	4526
Max:	4743	5614
	4758	5005
Break:	4396	5004
	3695	5040
<u>Modulus, kpsi</u>		
	611.1	520.3
	613.0	513.9
<u>Elongation, % at break</u>		
	355	433
	315	400

IZOD IMPACT, ft. lb. /in. of notch

<u>Bar Direction</u>	<u>Perpendicular to Bar Direction</u>
24.8	26.1
22.0	25.0

EXAMPLE 10

Effect of Sequence of Heat-treatment, Cooling, Reheating to a Lower Temperature, and Pressure Recrystallization on UHMWPE.

- 5 A UHMW PE bar (3" x 15") of the same type as in Example 1 was heated for five hours at 325°C under N<sub>2</sub>, then slowly cooled to room temperature. It was reheated to 225°C, and pressure recrystallized as described in Example 9 according to the following schedule:

241° to 191°C	300 MPa	2 hours, 15 minutes
191° to 181°C	300 MPa	2 hours
181° to 171°C	300 MPa	6 hours

The resulting product was machined into test pieces and analyzed with the following results:

DSC

	<u>Center of Bar</u>	<u>1 cm in from Bar Edge</u>
<u>m.p., °C</u>		
1st heat	149.3	149.1
2nd heat	134.3	135.2
$\Delta T$	15	13.9

Heat of Fusion

1st heat	223.6 J/g	229.6 J/g
2nd heat	156.1 J/g	162.3 J/g

Infrared Crystallinity Index

In Bar Direction	0.745
Perpendicular to Bar Direction	0.759

Tensile Properties

<u>Stress, psi</u>		
At Yield	4706	4463
At Break	5362	5326
<u>Modulus, kpsi</u>	649.7	404.2
<u>Elongation, %</u>		
At Yield	4.7	4.5
At Break	330	335
<u>Deformation (Creep)</u>		
(% at 1000 psi load)		

0.4

0.3

Effect of Preheating by Reflux

5 The preliminary heating of this example may be achieved in an atmosphere of refluxing vapors instead of N<sub>2</sub>, as described below.

10 A 3" x 18" rod of UHMWPE (American Hoechst, Hostalen GUR 415) was heated in refluxing vapors of Krytox®-143AZ (E. I. du Pont de Nemours and Company, Wilmington, Delaware) (at 333-335°C) for 2 hours, 40

minutes. Krytox®-143AZ is a perfluoroalkylpolyether that is a nonflammable, chemically inert liquid having unusually high thermal and oxidative stability. Vapors of other liquids demonstrating these characteristics may also be suitable. The overall system was wrapped with glass insulation to facilitate slow cooling and protected by a nitrogen atmosphere. As compared to the starting material, the resulting product has improved crystallinity (IRCI from 0.27 to 0.47), a tensile modulus (from 210 kpsi to 300 kpsi), and tensile strength at yield (from 3400 to 3850 psi). Most significantly, the product displays a large increase in elongation at break (from 315% to 893%).

When the above described material was recrystallized from 220°C under 300 MPa, a new polyethylene resulted possessing extremely high elongation at break (667%) along with the high tensile strength at yield (4900 psi) and the tensile modulus (574 kpsi) expected of the superior, enhanced UHMWPE materials.

Flex Modulus, kpsi	436.4
	431.2
	433.80 (av)
Density	.9684
IZOD IMPACT,	
(ft.lb./in. of notch)	17.1
	15.9
	16.5 (av)

#### EXAMPLE 11

##### Effect of Heating Temperature on UHMW PE

Cubes (3/4") of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabricated by Westlake) were wrapped in Teflon® film and placed in a large test tube protected from air with N<sub>2</sub>. A small thermocouple was inserted into the center of one of the cubes to

determine the time necessary for the samples to reach test temperature. A plug of glass wool was placed above the sample to control convection currents. The tube was heated with a Wood's metal bath. After the heat treatment was complete, the samples were wrapped in insulation to ensure slow cooling. At a bath temperature of 250°C, the samples required 45 minutes to reach test temperature.

Time Sample at Temperature <u>hrs:min</u>	Test Temperature <u>°C</u>	Crystallinity Index <u>(by IR)</u>
4:00	250	0.232
20:00	250	0.244
4:00	293	0.264
:01	293	0.230
4:00*	320-325	0.374
1:00*	334-335	0.378
1:00*	340-342	0.391

\*Heated by submerging sample wrapped in Teflon® film under Woods metal as described in the following paragraph.

#### Effect of Time on Heating UHMW PE

Small cubes (3/4") of UHMW PE cut from the rod form of Hoechst Hostalen GUR 415 were wrapped in Teflon® film, tied to a glass rod, and pushed under the surface of a Wood's metal bath. A small thermocouple was inserted in one of the cubes; when plunged into a 322-329°C bath, twelve minutes were required for the sample center to reach 321°C. The time at temperature (not the time in the bath) is recorded below. The samples were removed from the bath and wrapped in glass fiber insulation to permit slow cooling which required 1.5 hours to reach 80°C. The extent of change was determined by measuring crystallinity indices.

Time Sample at 320-325°C (hrs:min)	Crystallinity Index by (IR)
no heating	.258
0:10	.261
0:20	.294
1:00	.330
4:00	.374

Heat Treatment of UHMW PE (Large Scale)

A 3" diameter by 18" bar of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabrication by Westlake) was heated under nitrogen at 325°C for 4 hours (65B). The bar was cut into test pieces as was a bar of the same starting polymer that had not been treated. Tests were run sequentially:

	Untreated Polymer	Thermally Treated	% Difference
<u>DSC</u>		sharper (narrow curve)	
m.p.°C	139.7	137.5	
Heat of Fusion J/g	154.6	197.5	+28
Crystallinity Index (IR)	0.258	0.386	+50

Tensile Properties

Stress, psi	3380	3694	
	3456	3642	
	3418 (av)	3668 (av)	+7.3
Max.	5361	4706	
	4864	4673	
	5113 (av)	4690 (av)	
Break	5361	4705	
	4864	4673	
	5113 (av)	4689 (av)	

Elongation, % Break

	330	490	
	300	500	
	315 (av)	495 (av)	+57
Modulus, kpsi	208.4	244.6	
	210.5	253.7	
	209.5 (av)	249.1 (av)	+19

Flex Modulus, kpsi

	124.4	151.5	
	137.1	146.8	
	130.7 (av)	149.1 (av)	+14

IZOD IMPACT, (ft.lb./in. of notch)

	15.93	19.97	
	20.81	22.68	
	18.37 (av)	21.32 (av)	+16

Deformation (Creep) (% at 1000 psi load)

	1.8	1.6	-17
	1.7	1.3	

Similarly, a 3" diameter bar of different UHMW polyethylene (Himont 1900, m.w. 1,000,000) was heat pretreated in an inert atmosphere, for example, of N<sub>2</sub>. The product had greatly improved elongation and impact resistance.

5

	<u>Untreated Polymer</u>	<u>Thermally Treated</u>	<u>% Difference</u>
<u>DSC</u>			
Heat of Fusion J/g	166.3	190.7	+15
Crystallinity Index (IR)	.284	.379	+33

Tensile PropertiesStress, psi

Yield	3544	3721	
	3703	3589	
	3622 (av)	3655 (av)	-0

29

Max.	7387	6545	
	7190	5999	
	7289 (av)	6272 (av)	-14
Elongation, %, Break			
	200	343	
	216	293	
	208 (av)	318 (av)	+53
Elongation, %, Yield			
	16.6	20	
	20	16.6	
Modulus, kpsi	128.4	212.7	
	216.2	192.7	
	202.7 (av)	202.7 (av)	0
<u>IZOD Impact</u> , (ft.lb./in. of notch)			
	13.05	24.26	
	11.94	17.12	
	12.49 (av)	21.09 (av)	+65

Effect of 4 Hour Heating at Higher Temperatures

Sample bars (18" x 3" diameter) of UHMWPE (Hoechst Hostalen GUR 415, fabricated by Westlake) were heated in an oven under nitrogen for 4 hours at the temperatures shown below, then cooled to room temperature and tested.

TENSILE PROPERTIES

Temp. °C	Crysty. Index	IZOD ftlb/in of notch	Yield psi	Modulus kpsi	Elong(b) %
as is	0.26	18.4	3400	210	315
325	0.386	22.7	3700	250	495
334	0.47	21.8	3900	300	893
342	0.514	20.7	4100	240	1100
349	0.570	16.8	4200	250	1335
355	0.602	2.1	4200	280	1630

The results show a startling improvement in properties following a 4 hour heat treatment at temperatures above 320°C.

EXAMPLE 12

A 3" diameter bar (rod), 18" in length, of American Hoechst Hostalen GUR 415 ultrahigh molecular weight polyethylene, was heated in an oven and then encapsulated with low molecular weight polyethylene by rolling the hot rod onto a 1/16" sheet of low molecular weight polyethylene heated to 180°C on a large hot plate. An intervening sheet of "Teflon" Polytetrafluoroethylene film was kept on the encapsulated rod to prevent sticking to the hot plate. The rod ends were similarly sealed. The "Teflon" film was kept on the encapsulated rod to prevent sticking in the reactor.

The bar was heated to 225°C under a nitrogen atmosphere and transferred to the reactor at 225°C. After sealing, the reactor pressure was taken to 300 MPa which caused the temperature to reach 237°C. The reactor was permitted to cool to 180°C in 6.5 h, then maintained at this temperature for 1h. The temperature was dropped to 170°C, held at this temperature for 3h, then cooled slowly to 150°C from where it was cooled rapidly.

The rod, which remained coated, was cut and machined into two test pieces (A and B) which gave the following results:

	<u>SAMPLE</u>	
<u>DSC</u>	A	B
<u>1st Heat:</u>		
Melt point, °C	149.1	153.7
Heat of Fusion, J/g	219.8	209.5
<u>2nd Heat:</u>		
Melt point, °C	135.5	136.6
Heat of Fusion, J/g	141.2	144.9
<u>Crystallinity Index (IR)</u>	0.566	0.567



Tensile Properties:

Stress, psi		
At Yield	4149	4076
At Max.	7448	8138
At Break	7448	8138
Elongation, %	323	346
Modulus, kpsi	363.6	358.2
Creep, %	0.6	0.6
IZOD Impact,	15.9	15.8
(ftlb/in. of notch)		

EXAMPLE 13

A 5.75" segment of enhanced ultrahigh molecular weight polyethylene prepared as in Example 5, was skived to two films (A and B), of 11 mil and 5 mil thickness, respectively. The following properties were obtained (averaged from five tests per film sample):

SAMPLE

	A	B
<u>Tensile Properties:</u>		
Stress, psi		
At Yield	3035	3108
At Max.	6554	4083
At Break	6481	4083
At 5% Elongation	2667	2705
Modulus, kpsi	129.7	165.6
Elongation at Break, %	470	237.6

The skived films were hot drawn in a tenter frame at 140°C. One piece of the 5 mil film was drawn 6 fold in one direction (C). A second piece of the 5 mil film was drawn 3 fold in both directions (D):

SAMPLE

	C	D
<u>Tensile Stress, psi</u>		
At Yield	37,819	13,720
At Max.	42,058	19,358

At Break	46,426	18,995
Tensile Modulus, kpsi	93.3	94.9
Elongation at Break, %	56	132.4
Thickness, mils	2.6	1.6

#### CONTROL

In this experiment, a product was prepared in the manner of Example 1 of U.S. Patent No. 3,944,536.

- A sample of the ultrahigh molecular weight polyethylene used in Example 1 previously described herein, measuring 1/4" x 1/4" x 1/8" thick was heated between a film of polytetrafluoroethylene on a hot plate at atmospheric pressure and at a temperature of 160°C on the upper side and 270°C on the lower side.
- The molten sample was transferred quickly to a hydraulic press at room temperature where the sample was subjected to a pressure of 8 tons (about 250,000 psi or about 1600 MPa. It required 1.6 seconds to attain full pressure. The resulting polymer was tested. It displayed an infrared crystallinity index of 0.199. Its melting point was 134.5°C and, when reheated, 134.4°C.

#### EXAMPLE 14

- Two bars (18" x 3" diameter) of UHMWPE (Hoechst Hostalen GUR 415, fabricated by Westlake) were heat-treated in a forced N<sub>2</sub> oven at 335°C to 345°C for 4 hours. The oven was slowly cooled to room temperature.

- One bar was placed in a pressure vessel and heated at 220°C for 2 hours before being pressured to 300 MPa with water as pressure transfer fluid. The temperature was allowed to cool to 185°C for 2 hours, allowed to cool to 174°C, held for 2 hours at this temperature, cooled over 5 hours to 150°C, then cooled rapidly to 90°C. All cooling was carried out under 300 MPa pressure.

- Test pieces were cut from both bars and tested with the following results:

	Heat <u>Only</u>	Heat, Pressure <u>Recryst.</u>
<u>DSC</u>		
M.P. °C		
1st heat	139.7	147.9
2nd heat	134.7	136.1
Heat of Fusion, J/g		
1st heat	211.2	245.8
2nd heat	182.5	188.8
<u>Tensile Properties</u>		
Stress, psi		
Yield	3930	4778
Max	6023	5117
Break	5779	5102
Modulus, kpsi		415.2
Elongation, %		
Yield	18	7
Break	920	532
<u>IZOD Impact</u>		
ftlb/in of notch	22.6	22.2
<u>Crystallinity Index</u>	0.446	0.812

EXAMPLE 15

A reactor with a configuration similar to that shown in Figure 2 having an internal diameter of 5" and a length of approximately 70" was charged with a 4" x 60" rod of Hoechst Hostalen GUR 415 UHMWPE manufactured by Poly Hi, Inc. The closed vessel was evacuated, filled with water, and heated to 250°C over a period of 1.5 h. This temperature was maintained for an additional 2 h to insure that the UHMWPE rod was heated uniformly and no significant temperature gradients were present. The pressure was then raised to 33,000 psi (228 MPa). This pressure was maintained for the duration of the experiment. After 1 h, the temperature was ramped down to 175°C over a period of 3 h (cooling

rate approximately 25°C/h). The temperature of 175°C was maintained for 1 h, and the reactor was then cooled to 75°C over a period of 2 h. The pressure was then released, and the rod was removed from the autoclave.

5 A 12" length was cut from the rod for evaluation.

A sample from the center of the rod was used for DSC analysis. The melting curve showed two peaks, one at 139°C and one at 148°C, with the higher peak being the larger. When the sample was cooled and reheated, a  
10 single melting peak at 135°C was observed. Samples from the center of the rod had a density of 0.946 g/ml and a crystallinity index (IRCI) of 0.354. ASTM Type I tensile specimens were prepared from the rod, and the following test results were obtained:

15	Modulus (kpsi)	329
	Tensile Stress (yield, kpsi)	3.79
	Tensile Stress (break, kpsi)	4.94
	Elongation, %	334

Creep specimens in the form of 0.5" cubes were also  
20 prepared from the center of the rod. A creep of 1.4% was observed under 1000 psi load.

#### EXAMPLES 16-22

The procedure of Example 15 was employed in the subsequent examples, except that in Examples 16, 18 and  
25 21 the Hoechst Hostalen GUR 415 UHMWPE rod dimensions were 3" x 60". The enhancement temperature in each example was 250°C. Enhancement pressure and properties, determined as previously described, are given in the table below.

Ex.	Press (kpsi)	Modulus (kpsi)	TS(Y) (kpsi)	TS(B) (kpsi)	Creep (%)	IRCI	Density (g/ml)
16	33	295	3.69	4.82	1.4	0.333	0.943
17	29	280	3.50	4.82		0.304	0.940
18	29	255	3.51	4.68		0.281	0.938
19	35	361	3.96	5.53	1.2	0.373	0.949
20	37	405	4.12	5.53	0.97	0.401	0.951
21	37	364	3.98	5.30		0.410	0.951
22	39	424	4.12	5.56	0.95	0.419	0.951

The products of Examples 16-22 each display two peaks in their DSC meeting point curves. This bimodal characteristic indicates that Examples 16-22 are composites of the extended chain form of the higher molecular weight fraction of the polymer and of the folded chain form of the lower molecular weight fraction of the polymer. The results of Examples 16-22 further indicate that compositions may be altered by choice of polyethylene of different weight and molecular distributions.

CLAIMS

What is claimed is:

1. An ultrahigh molecular weight linear polyethylene having a molecular weight of at least 400,000, a crystalline melting point of greater than 144°C, the reduction in said melting point upon remelting being greater than 11°C, an infrared crystallinity of at least about 0.28, and a crystal morphology comprising a bimodal distribution of molecular chain fold spacings, one group of said from 2,000 to 8,000 Angstroms, the other group being from 50 to 500 Angstroms.
2. The polyethylene of Claim 1 exhibiting a flexural modulus of 250-500 kpsi, a tensile stress at yield of 3.5-4.5 kpsi, a tensile stress at break of 4-9 kpsi, a tensile modulus of 250-700 kpsi, an elongation at break of 200-500%, a notched Izod impact resistance of 12-25 ft.lb. per in. of notch and a creep at a compression of 1 kpsi of less than 1.4% after 24 hours at a temperature of 23°C and a relative humidity of 50%.
3. The polyethylene of Claim 2 wherein the tensile modulus is 250-600 kpsi, the notched Izod impact resistance is 12-20 ft.lb. per inch of notch and the infrared crystallinity index is at least 0.5.
4. An article consisting essentially of the polyethylene of Claim 2.
5. The article of Claim 4 wherein its dimensions are at least one inch by at least one inch.
6. The article of Claim 4 wherein its smallest dimension is at least 0.2 inch.
7. A process for preparing the polyethylene of Claim 2 consisting essentially of the following steps:
  - (a) forming an article of an ultrahigh molecular weight linear polyethylene having a molecular weight of at least 400,000;

(b) subjecting said article to a fluid under pressure of at least 200 MPa and a temperature of 190°-300°C for at least 0.5 hour;

(c) reducing the temperature to about  
5 160-170°C or lower while maintaining the pressure at at least 200 MPa, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and

(d) cooling to a temperature of about 130°C  
10 or lower and reducing the pressure to about 100 kPa in a manner such that remelting of said article is prevented.

8. The process of Claim 7 wherein step (a) is performed after step (d).

9. The process of Claim 7 wherein said fluid is  
15 water.

10. The process of Claim 7 wherein said pressure in step (b) is at least 300 MPa.

11. The process of Claim 7 wherein said temperature in step (b) is 200°-260°C.

20 12. The process of Claim 7 wherein the temperature and pressure in step (d) is maintained for at least one hour.

13. The process of Claim 7 wherein the surface of the article is shaved after step (d).

25 14. The process of Claim 7 wherein the cooling rate in step (c) is no greater than 35°C per hour.

15. The process of Claim 14 wherein the cooling rate in step (c) is no greater than 10°C per hour.

30 16. The polyethylene of Claim 1 wherein the flexural modulus is 250-650 kpsi, the tensile stress at yield is 3.5-5.4 kpsi, the tensile stress at break is 4-6 kpsi, the tensile modulus is 250-700 kpsi, the elongation at break is 200-600%, the notched IZOD impact resistance is 12-25 ft.lb. per inch of notch and creep  
35 at a compression of 1 kpsi is less than 1% after 24

hours at a temperature of 23°C and a relative humidity of 50%.

17. The polyethylene of Claim 16 wherein the tensile modulus is 250-650 kpsi and the infrared crystallinity is at least 0.5.

18. An article consisting essentially of the polyethylene of Claim 16.

19. The article of Claim 18 wherein its dimensions are at least one inch by at least one inch.

20. The article of Claim 18 wherein its smallest dimension is at least 0.2 inch.

21. A process for preparing the polyethylene of Claim 16 consisting essentially of the following steps:

(a) forming an article of an ultrahigh molecular weight linear polyethylene having a molecular weight of at least 400,000;

(b) subjecting said article to a preliminary heat treatment at a temperature of 280°-355°C, in an inert atmosphere for at least 0.5 hour;

(c) subjecting said article to a fluid under pressure of at least 280 MPa and a temperature of 190°-300°C for at least 0.5 hour;

(d) reducing the temperature to 160°-170°C or lower while maintaining the pressure at at least 280 MPa, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and

(e) cooling to a temperature of about 130°C or lower and reducing the pressure to approximately 100 kPa in a manner such that remelting of said article is prevented.

22. The process of Claim 21 wherein step (a) is performed after step (e).

23. The process of Claim 21 wherein said fluid is water.



24. The process of Claim 21 wherein said heat treatment in step (b) is continued for at least 3 hours at a temperature of at least 320°C.

25. The process of Claim 21 wherein said pressure  
5 in step (c) is at least 300 MPa.

26. The process of Claim 21 wherein said temperature in step (c) is 200°-300°C.

27. The process of Claim 21 wherein the temperature and pressure in step (e) are maintained for  
10 at least one hour.

28. The process of Claim 21 wherein the surface of the article is shaved after step (e).

29. The process of Claim 21 wherein the cooling rate in step (d) is no greater than 35°C per hour.

15 30. The process of Claim 29 wherein the cooling rate in step (d) is no greater than 10°C per hour.

31. An improved folded chain ultrahigh molecular weight linear polyethylene having a molecular weight of at least 400,000, and exhibiting a flexural modulus of  
20 150-300 kpsi, a tensile stress at yield of 3.5-4.3 kpsi, a tensile stress at break of 4-6 kpsi, a tensile modulus of 150-300 kpsi, a notched Izod impact resistance of 15-25 ft.lb. per in. of notch, an elongation at break of 200-1400%, a creep at a compression of 1 kpsi of less  
25 than 2% after 24 hours at a temperature of 23°C and a relative humidity of 50%, and an infrared crystallinity index of at least about 0.35.

32. The polyethylene of Claim 31 having a molecular weight of at least 1,000,000.

30 33. An article consisting essentially of the polyethylene of Claim 31.

34. The article of Claim 33 wherein its dimensions are at least one inch by at least one inch.

35 35. The article of Claim 33 wherein its smallest dimension is at least 0.2 inch.

36. A process for preparing the polyethylene of Claim 31 consisting essentially of the following steps:

(a) forming an article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000;

(b) subjecting said article to a temperature of 280°-355°C in an inert atmosphere for at least 0.5 hour;

(c) cooling the article non-precipitously to a temperature of about 130°C or below.

37. The process of Claim 36 wherein step (a) is performed after step (c).

38. The process of Claim 36 wherein said temperature in step (b) is 320°-350°C.

39. The process of Claim 36 wherein the temperature in step (b) is maintained for at least one hour.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/10005

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A61F2/32; A61L27/00; C08L23/06		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	A61F ; A61L ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 373 800 (E. I. DU PONT DE NEMOURS) 20 June 1990 see page 4, line 56 - page 5, line 16; claims 1-59; example 1 ---	1-39
X	EP,A,0 290 141 (MITSUI PETROCHEMICAL) 9 November 1988 see page 5, line 6 - line 31; figures 1-5 ---	1
A	JOURNAL OF POLYMER SCIENCE, POLYMER PHYSICS EDITION vol. 7, 1969, NEW YORK US pages 2051 - 2059 DAVIDSON & WUNDERLICH 'Extended-chain crystals. II. Crystallisation of polyethylene under elevated pressure.' see page 2052, line 32 - line 38 -----	1
<p><sup>10</sup> Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
24 MARCH 1993		14.05.93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer R. E. Goovaerts

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210005  
SA 67429

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0373800	20-06-90	CA-A- 2004454	02-06-90
		EP-A- 0446300	18-09-91
		JP-T- 4502028	09-04-92
		WO-A- 9006139	14-06-90
EP-A-0290141	09-11-88	JP-A- 63275708	14-11-88
		JP-A- 63275709	14-11-88
		JP-A- 63275710	14-11-88
		JP-A- 63275711	14-11-88
		AU-B- 618257	19-12-91
		US-A- 5115067	19-05-92

EPO FORM P007

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**